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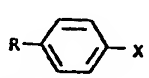
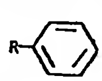
(54) Process for producing a halobenzene.

(57) A process for producing a halobenzene represented by the formula:



(I)

where R is a lower alkyl group, a lower alkoxy group or a halogen atom, and X is a halogen atom, which comprises halogenating a benzene represented by the formula:



(II)

where R is as defined above, in a liquid phase in the presence of a catalyst, characterized in that the catalyst is a combination of an aliphatic carboxylic acid component and a zeolite having a SiO_2/Al_2O_3 molar ratio of from 3 to 8 and a pore size of from 6 to 10 Å.

EP 0 154 236 A1

PROCESS FOR PRODUCING A HALOBENZENE

The present invention relates to a process for producing a halobenzene such as chlorotoluene or dichlorobenzene which is useful as a starting material for the production of medicines and agricultural chemicals. More particularly, it relates to a process for producing a p-halobenzene with high selectivity by halogenating a benzene with use of a novel catalyst.

Halobenzenes are useful as starting materials for medicines and agricultural chemicals. Particularly, there are strong demands for p-halobenzenes among them. Accordingly, there have been various studies to improve the selectivity for p-halogenation.

As a process for the liquid phase halogenation of an alkyl benzene, it has been common to conduct the halogenation in the presence of a Lewis acid catalyst such as antimony chloride, ferric chloride or aluminum chloride by means of a halogenating agent such as chlorine gas. However, such a process produces an o-chloroalkylbenzene as a major product and a m-chloro derivative and a polychloro derivative as by-products,

whereby it is impossible to produce a p-chloroalkylbenzene in good selectivity as high as at least 40%. Under the circumstances, there have been various researches for the developments of catalysts to improve the selectivity for a p-chloroalkylbenzene, and there have been some proposals.

For example, there have been known a method wherein a p-chloro derivative is obtained in a selectivity of from 45 to 52% by means of a catalyst composed of a Lewis acid and sulfur or selenium, a method wherein a p-chloro derivative is obtained in a selectivity of from 55 to 60% by means of a catalyst composed of a Lewis acid and thianthrene (U.S. Patent 4,031,147), and a method wherein a p-chloro derivative is obtained in a selectivity of from 52 to 60% by means of a catalyst system composed of a Lewis acid and a phenoxthine compound (U.S. Patent 4,444,983). On the other hand, with respect to chlorination of chlorobenzene, there have been known a method wherein p-dichlorobenzene is obtained in a selectivity of from 60 to 70% by reacting chlorobenzene with chlorine in the presence of an iron sulfide catalyst (GB 1,476,398), and a method wherein a p-dichlorobenzene is obtained in a selectivity of 72% by reacting chlorobenzene with chlorine by means of selenium or a selenium compound as a catalyst (Japanese Examined Patent Publication No. 34010/1975).

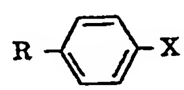
However, these conventional methods are not necessarily satisfactory as a process for the production

of a p-halobenzene, because the selectivity for the p-halo derivative is low in each case.

Accordingly, it is an object of the present invention to provide a process for producing a p-halobenzene in high selectivity by a liquid phase halogenation of a benzene in the presence of a catalyst.

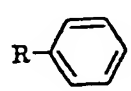
It has been found that the object of the present invention can be attained by using as the catalyst a combination of an aliphatic carboxylic acid component and a certain zeolite. The present invention is based on this discovery.

Namely, the present invention provides a process for producing a halobenzene represented by the formula:



(I)

where R is a lower alkyl group, a lower alkoxy group or a halogen atom, and X is a halogen atom, which comprises halogenating a benzene represented by the formula:



(II)

where R is as defined above, in a liquid phase in the presence of a catalyst, characterized in that the catalyst is a combination of an aliphatic carboxylic acid component and a zeolite having a SiO_2/Al_2O_3 molar ratio of from 3 to 8 and a pore size of from 6 to 10 Å.

Now, the present invention will be described in detail with reference to the preferred embodiments.

As the substituents R in the starting compound of the formula II used in the process of the present invention, there may be mentioned a straight chained or branched alkyl or alkoxy group, or a halogen atom such as a fluorine atom, a chlorine atom or an bromine atom. Particularly preferred is an alkyl group having from 1 to 4 carbon atoms or a chlorine atom.

In the process of the present invention, it is essential to use as the catalyst a combination of an aliphatic carboxylic acid component and a zeolite having a SiO_2/Al_2O_3 molar ratio of from 3 to 8 and a pore size of from 6 to 10 Å. When a zeolite with a SiO_2/Al_2O_3 molar ratio or a pore size being outside the above-mentioned range, is used, the selectivity for a p-halobenzene will be substantially poor.

A typical representative of the zeolite which satisfies the above conditions, is L-type zeolite, which is a crystalline aluminosilicate having a SiO_2/Al_2O_3 molar ratio of from 4 to 8 and a pore size of from about 7 to about 10 Å. As another example of the zeolite which satisfies the above conditions, there may be mentioned Y-type zeolite having a SiO_2/Al_2O_3 molar ratio of from 3 to 7 and a pore size of from about 6 to about 9 Å.

For the catalyst of the present invention, it is also possible to employ a synthetic zeolite or natural zeolite having the same X-ray diffraction spectrum as the above-mentioned L-type or Y-type zeolite. Further, the ion

exchangeable cations contained in such zeolite are usually sodium or potassium, but may further include other cations. As such cations, there may be mentioned metal ions or protons belonging to Group IA, Group IIA, Group IIIA, Group IVA or Group VA of the periodic table. These cations may be of the same type or of two or more different types.

For the purpose of the present invention, the term "aliphatic carboxylic acid component" includes an aliphatic carboxylic acid and its derivatives such as a halide, anhydride or metal salt of an aliphatic carboxylic acid. As the aliphatic carboxylic acid, there may be mentioned acetic acid, propionic acid, isovaleric acid, monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, α-chloro-propionic acid, β-chloropropionic acid, difluoroacetic acid, trifluoroacetic acid, pentafluoropropionic acid or β-chloro-tetrafluoropropionic acid which may be substituted or unsubstituted. The metal salt may be a sodium, potassium or barium salt of an aliphatic carboxylic acid. The halide may be a chloride or a bromide of an aliphatic carboxylic acid. Among them, aliphatic carboxylic acids and their metal salts are preferred. Among them, sodium salts or potassium salts are further preferred. Further, aliphatic carboxylic acids and their metal salts may be employed in the form of hydrates.

The aliphatic carboxylic acid component is used in an amount of at least 1% by weight relative to the zeolite. However, from the industrial point of view, it is preferred to use the aliphatic carboxylic acid component in an amount within a range of from 3 to 30% by weight relative to the zeolite.

In the present invention, the zeolite and the aliphatic carboxylic acid component may be combined prior to the halogenation reaction. Alternatively, the zeolite and the aliphatic carboxylic acid component may simultaneously be added to the reaction system at the time of the halogenation.

The premixing may be conducted in such a manner that the zeolite is suspended in a solvent, a predetermined amount of the aliphatic carboxylic acid component is added thereto, then, the solvent is distilled off and the mixture is dried under reduced pressure.

On the other hand, in the case of combining them at the time of the reaction, the zeolite is suspended in the starting matreial benzene fed in the halogenation reactor, then a predetermined amount of the aliphatic carboxylic acid component is added thereto, and the mixture is stirred at a temperature lower than the boiling point, preferably from 20 to 100°C, followed by the subsequent halogenation.

The combination of the zeolite and the aliphatic carboxylic acid component can be adequately conducted by

one of the above methods. However, if desired, both methods may be employed for the adequate treatment of the zeolite with the aliphatic carboxylic acid component.

To conduct the halogenation of a benzene in accordance with the process of the present invention, for instance, the zeolite treated with the aliphatic carboxylic acid component is added in an amount of at least 0.01 g, preferably from 0.1 to 10 g, per mol of the starting material benzene, and a halogenating agent is introduced into the mixture in a liquid phase while stirring the mixture at a temperature of not higher than the boiling point. In this operation, a reaction solvent may be employed as the case requires. As the halogenating agent, there may be employed any agent commonly employed for the halogenation of aromatic rings. Preferred are chlorine, bromine and sulfuryl chloride. These halogenating agents may be employed as diluted with an inert gas such as nitrogen. The reaction temperature for the halogenation is usually from 0°C to the boiling point of the reaction mixture, preferably from 20 to 100°C from the practical viewpoint. The reaction may be conducted under reduced or elevated pressure, but is usually conducted under atmospheric pressure.

According to the process of the present invention, it is possible to selectively and efficiently halogenate the p-position of the benzene of the formula II while suppressing the halogenation at the o-position, and to

minimize the formation of by-products such as side chain-halogenated products or polyhalogenated products, whereby a highly useful p-halobenzene of the formula I can be obtained in good selectivity.

Further, according to the process of the present invention, in a case where a p-dihalobenzene is to be produced from a monohalobenzene as the starting material, it is possible to advantageously conduct the production of the monohalobenzene from benzene and the step of halogenating the monohalobenzene to the p-dihalobenzene, continuously in the same reactor.

Furthermore, according to the process of the present invention, the operation of the reaction and the subsequent after-treatment is simple, and the catalyst can be reused. Thus, the process of the present invention is suitable as an industrial process for the production of p-halobenzenes.

Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted by these specific Examples.

EXAMPLE 1

Into a 200 ml reaction flask equipped with a condenser, a thermometer, a stirrer and a gas supply tube, 5 g of L-type zeolite (tradename: TSZ-506, manufactured by Toyo Soda Manufacturing Co., Ltd.) and 92.1 g (1 mol) of toluene were introduced, and 1.0 g of

monochloroacetic acid was added thereto. The mixture was maintained at 70°C, and stirred for 30 minutes while supplying nitrogen gas. Then, chlorine gas was supplied at a rate of 0.25 mol/hr for 4 hours to conduct the reaction while maintaining the reaction temperature at 70°C. After the completion of the reaction, the reaction product thereby obtained, was analyzed by gas chromatography, whereby it was found that the conversion of toluene was 98.3%, the production ratio of o-chlorotoluene/p-chlorotoluene (hereinafter referred to simply as "o/p ratio") was 0.262, and the selectivity of p-chlorotoluene was 74.2%.

EXAMPLE 2

The reaction was conducted in the same manner as in Example 1 except that monochloroacetic acid was added in an amount of 0.25 g, whereby the conversion of toluene was 95.3% and the o/p ratio was 0.269.

EXAMPLES 3 to 13 and COMPARATIVE EXAMPLES 1 and 2

The halogenation was conducted in the same manner as in Example 1 except that a various substituted or unsubstituted aliphatic carboxylic acid as identified in Table 1 was used instead of monochloroacetic acid, and the temperature for the treatment of the zeolite and the reaction temperature were adjusted to 50°C, 70°C or 90°C. The results are shown in Table 1.

Further, for the purpose of comparison, the Table includes the results obtained from the cases wherein

L-type zeolite as catalyst, and a combination of L-type zeolite with benzoic acid were employed.

Table 1

Example	Aliphatic carboxylic acid	Zeolite treating temp. & reaction temp. (°C)	Conversion (%)	o/p ratio
3	Acetic acid	70	99.8	0.319
4	α-Chloropropionic acid	70	93.8	0.233
5	β-Chloropropionic acid	70	90.4	0.220
6	β-Chloropropionic acid	90	92.0	0.325
7	Dichloroacetic acid	70	96.2	0.250
8	Difluoroacetic acid	70	95.4	0.250
9	Trifluoroacetic acid	70	99.7	0.344
10	Propionic acid	50	90.6	0.254
11	Monobromoacetic acid	50	99.4	0.248
12	Monochlorodifluoroacetic acid	50	99.8	0.248
13	Pentafluoropropionic acid	50	99.8	0.296
Comparative 1	None	70	95.1	0.496
Comparative 2	Benzoic acid	70	93.9	0.608

EXAMPLE 14

The halogenation was conducted in the same manner as in Example 1 except that 112.6 g (1 mol) of chlorobenzene was used as the starting material instead of toluene, dichloroacetic acid was used instead of monochloroacetic acid, and the reaction time was changed to 5 hours, whereby the conversion of chlorobenzene was 90.5%,

the production ratio of o-dichlorobenzene/p-dichlorobenzene was 0.071, and the selectivity of p-dichlorobenzene was 92.7%.

EXAMPLE 15

The halogenation was conducted in the same manner as in Example 1 except that Y-type zeolite (tradename: LZ-Y82, manufactured by Union Carbide Corp., U.S.A.) was used instead of L-type zeolite, 108.1 g (1 mol) of anisole was used as the starting material instead of toluene, and difluoroacetic acid was used instead of monochloroacetic acid, whereby the conversion of anisole was 91.5%, and the production ratio of o-chloroanisole/p-chloroanisole was 0.218.

EXAMPLE 16

After the completion of the reaction in Example 1, the catalyst was recovered from the reaction mixture. By using the recovered catalyst, the halogenation was repeated 4 times in the same manner as in Example 1, whereby the reaction proceeded normally in each case and the conversion was 98.1% and the o/p ratio was 0.267.

EXAMPLE 17

Into a 200 ml reaction flask equipped with a condenser, thermometer, a stirrer and a gas supply tube, 5 g of L-type zeolite (tradename: TSZ-506, manufactured by Toyo Soda Manufacturing Co., Ltd.) and 92.1 g (1 mol) of toluene were introduced, and 1.0 g of potassium dichloroacetate was added thereto. The mixture was maintained at 50°C and stirred for 30 minutes while

supplying nitrogen gas. Then, chlorine gas was supplied at a rate of 0.25 mol/hr for 4 hours to conduct the reaction while maintaining the reaction temperature at 50°C. After the completion of the reaction, the reaction product thereby obtained, was analyzed by gas chromatography, whereby it was found that the conversion of toluene was 96.6%, the o/p ratio was 0.208, and the selectivity of p-chlorotoluene was 79.63%.

EXAMPLES 18 to 22

The halogenation was conducted at 50°C in the same manner as in Example 17 except that a various metal salt of a substituted or unsubstituted aliphatic carboxylic acid, as identified in Table 2, was used instead of potassium dichloroacetate. The results are shown in Table 2.

Table 2

No.	Metal salt of an aliphatic carboxylic acid	Conversion (%)	o/p ratio
18	Potassium acetate	89.9	0.313
19	Sodium dichloroacetate	99.2	0.259
20	Potassium difluoroacetate	90.4	0.292
21	Barium acetate	91.9	0.322
22	Sodium acetate (trihydrate)	87.7	0.363

EXAMPLE 23

The halogenation was conducted in the same manner as in Example 17 except that 112.6 g (1 mol) of chlorobenzene was used as the starting material instead of toluene, and the reaction temperature was changed to 70°C, whereby the conversion of chlorobenzene was 90.5%, the production ratio of o-dichlorobenzene/p-dichlorobenzene was 0.062, and the selectivity of p-dichlorobenzene was 93.4%.

EXAMPLE 24

After the completion of the reaction in Example 23, the catalyst was recovered from the reaction mixture. By using the recovered catalyst, the operation was repeated 4 times in the same manner as in Example 23, whereby the reaction proceeded normally and the conversion was 90.1% and the production ratio of o-dichlorobenzene/p-dichlorobenzene was 0.075.

EXAMPLE 25

Into a 200 ml reaction flask equipped with a condenser, a thermometer, a stirrer and a gas supply tube, 5 g of L-type zeolite (tradename: TSZ-504, manufactured by Toyo Soda Manufacturing Co., Ltd.) and 92.1 g (1 mol) of toluene were introduced, and 0.5 g of chloroacetyl chloride was added thereto. The mixture was maintained at 50°C and stirred for 30 minutes while supplying nitrogen gas. Then, chlorine gas was supplied at a rate of 0.25 mol/hr for 4 hours to conduct the

reaction while maintaining the reaction temperature at 50°C. After the completion of the reaction, the reaction product thereby obtained was analyzed by gas chromatography, whereby the conversion of toluene was 98%, the o/p ratio was 0.312, and the selectivity of p-chlorotoluene was 70.38%.

EXAMPLE 26

The reaction was conducted in the same manner as in Example 25 except that chloroacetyl chloride was added in an amount of 0.25 g, whereby the conversion of toluene was 90.1% and the o/p ratio was 0.338.

EXAMPLES 27 to 32

The halogenation was conducted at 70°C in the same manner as Example 25 except that a various benzene as identified in Table 3 was used as the starting material instead of toluene. The results are shown in Table 3.

Table 3

No.	The benzene (II)	Conversion (%)	o/p ratio
27	Ethylbenzene	99.6	0.160
28	Cumene	94.6	0.108
29	t-Butylbenzene	95.9	0.036
30	Chlorobenzene	94.8	0.076
31	Anisole	89.0	0.192
32	Fluorobenzene	95.3	0.019

EXAMPLES 33 to 39

The halogenation was conducted at 70°C in the same manner as in Example 25 except that a various aliphatic carboxylic acid halide or anhydride as identified in Table 4 was used instead of chloroacetyl chloride used in Example 25. The results are shown in Table 4.

For the purpose of comparison, the table includes the results obtained by using a combination of L-type zeolite with benzoyl chloride (Comparative Example 3).

Table 4

No.	Aliphatic carboxylic acid derivative	Conversion (%)	o/p ratio
33	Trifluoroacetic anhydride	97.4	0.442
34	Acetic anhydride	86.3	0.409
35	Acetyl chloride	89.8	0.452
36	Chloroacetyl chloride	96.0	0.360
37	Dichloroacetyl chloride	85.2	0.438
38	Bromoacetyl chloride	82.3	0.442
39	Bromoacetyl bromide	79.7	0.437
Comparative Example 3	Benzoyl chloride	86.0	0.696

EXAMPLE 40

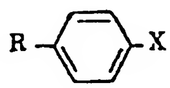
The halogenation was conducted at 70°C in the same manner as in Example 25 except that 35.2 g (1.0 mol) of sulfuryl chloride was dropwise added over a period of 4 hours instead of chlorine gas, and aging was conducted for 3 hours, whereby the conversion of toluene was 99.4% and the o/p ratio was 0.293.

EXAMPLE 41

After the completion of the reaction in Example 25, the catalyst was recovered from the reaction mixture. By using the recovered catalyst, the operation was repeated in the same manner as in Example 25, whereby the reaction proceeded normally, and the conversion was 98.2% and the o/p ratio was 0.320.

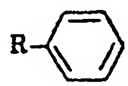
CLAIMS:

1. A process for producing a halobenzene represented by the formula:



(I)

where R is a lower alkyl group, a lower alkoxy group or a halogen atom, and X is a halogen atom, which comprises halogenating a benzene represented by the formula:



(II)

where R is as defined above, in a liquid phase in the presence of a catalyst, characterized in that the catalyst is a combination of an aliphatic carboxylic acid component and a zeolite having a SiO_2/Al_2O_3 molar ratio of from 3 to 8 and a pore size of from 6 to 10 Å.

2. The process according to Claim 1, wherein the aliphatic carboxylic acid component is an aliphatic carboxylic acid, or a halide, anhydride or metal salt thereof and preferably a sodium, potassium or barium salt of an aliphatic carboxylic acid.

3. The process according to one of Claims 1 or 2, wherein the aliphatic carboxylic acid component is an aliphatic carboxylic acid selected from the group consisting of acetic acid, propionic acid, isovaleric acid, monochloroacetic acid, monobromoacetic acid, dichloroacetic acid, trichloroacetic acid, α-chloropropionic acid, β-chloropropionic acid, difluoroacetic acid, trifluoroacetic acid, pentafluoropropionic acid and β-chloro-tetrafluoropropionic acid.

4. The process according to one of Claims 1 to 3, wherein the aliphatic carboxylic acid component is potassium dichloroacetate, sodium dichloroacetate or potassium difluoroacetate or chloroacetyl chloride.

5. The process according to one of Claims 1 to 4, wherein the zeolite is used in an amount of at least 0.01 g per mol of the benzene of the formula II and preferably in an amount of from 0.1 to 10 g per mol of the benzene of the formula II.

6. The process according to one of Claims 1 to 5, wherein the aliphatic carboxylic acid component is used in an amount of at least 1% by weight relative to the zeolite and preferably of from 3 to 30% by weight relative to the zeolite.

7. The process according to one of Claims 1 to 6, wherein the halogenation is conducted at a temperature within a range of from 0°C to the boiling point of the reaction mixture, and preferably at a temperature of from 20 to 100°C.

8. The process according to one of Claims 1 to 7, wherein R in the formulas I and II is an alkyl group having from 1 to 4 carbon atoms or a chlorine atom and wherein preferably the formula II represents toluene or chlorobenzene.

9. The process according to one of Claims 1 to 8, wherein the benzene of the formula II is chlorinated to obtain a halobenzene of the formula I where X is a chlorine atom.

10. The process according to one of claims 1 to 9, wherein the zeolite is L-type zeolite.

European Patent Office

EUROPEAN SEARCH REPORT

0154236
Application number

EP 85101707.9

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	JP - A - 57-77 631 (IHARA CHEMICAL KOGYO K.K.) * Example 1, table 1; page 2, left-hand column, lines 34-38 *	1,8,9	C 07 C 17/12 C 07 C 25/02 C 07 C 41/22 C 07 C 43/225
P,A	EP - A1 - 0 112 722 (IHARA CHEMICAL INDUSTRY CO.) * Claims; example 1 *	1,5,7-10	
A	PATENT ABSTRACTS OF JAPAN, unexamined applications, field C, vol. 7, no. 175, August 3, 1983 THE PATENT OFFICE JAPANESE GOVERNMENT page 134 C 179 * Kokai-no. 58-83 638 (IHARA CHEMICAL) *	1,7-9	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 07 C 17/00 C 07 C 25/00 C 07 C 41/00 C 07 C 43/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	15-05-1985	KÖRBER

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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